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NOx formation in laboratory investigations of oxy-coal combustion

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NOx formation was measured during pulverized coal and char combustion in N_2 and CO_2 environments under isothermal and nearly constant oxygen conditions (i.e. using dilute coal loading) at three different oxygen concentrations (12% O_2, 24% O_2, and 36% O_2) for a gas temperature of 1050 °C (1320 K). To separately investigate the importance of NO reburning under our low equivalence ratio conditions, experiments were also performed with an elevated level of NO in the gases into which the coal was introduced (550 ppm NO versus a typical baseline concentration of 30 ppm NO). This unique dataset should provide an unparalleled opportunity to understand and differentiate the different sources and sinks of NOx under oxy-fuel combustion conditions. For low levels of background NO, NOx production increases dramatically with bath gas oxygen content, for both N_2 and CO_2 environments, both in terms of absolute NOx concentrations and in terms of fractional fuel nitrogen conversion to NOx. These results highlight the importance of coal-N content and the volatile flame and char combustion temperatures on NOx formation. For the high background NOx condition, net NOx production is only observed in the 36% O_2 environment. Interestingly, NOx production is greater in CO_2 environments (relative to N_2 environments) at 12% O_2, but it is lower in CO_2 environments at 24% and 36% O_2.

1. Introduction

Oxy-fuel combustion of pulverized coal with recycled flue gas is a promising approach for continued use of coal for electric power production, while producing near-zero emissions of gases [1,2]. The nearly pure CO_2 product stream produced from this process is suitable for use in Enhanced Oil Recovery (EOR), Coal Bed Methane (CBM) production, or geologic sequestration. O_2/CO_2 recycle coal combustion technology is the only proposed zero-emission coal conversion technology that has the potential of being a retrofit technology for conventional pc boilers, taking advantage of the enormous capital investment represented by existing boilers. Also, O_2/CO_2 recycle combustion is a modification of the existing pc combustion technology that has well-proven reliability and industrial acceptance.

An important secondary benefit of O_2/CO_2 recycle combustion is a reduction in most pollutant emissions, particularly NOx. The level of concern over NOx in the exhaust from oxy-fuel combustion depends on several factors, including the level of compression and secondary cleaning of the flue gas required for subsequent CO_2 use or pipeline transport. In the near term, as the technology is being developed, it is important to fall below best-available control technology (BACT) emission standards for NOx because the flue gas will be exhausted to the atmosphere at times as the technology is being developed and perhaps even in the long run during system startup operation.

There have been a number of studies on NOx formation in O_2-recycle combustion using various reactors and burner configurations, including entrained flow reactors [3-7] and swirl burners [8-12]. These studies have shown varying levels of NOx reduction relative to pc combustion in air. NOx emissions are generally lower in O_2-recycle combustion because of negligible thermal NOx production (Zeldovich mechanism) from the use of a nearly N_2-free oxidizer and because of reburn of recycled NOx. However, elevated oxygen levels are generally used in O_2/CO_2 recycle combustion to maintain flame stability and furnace exit temperatures (i.e. boiler heat transfer) and very high concentrations of oxygen are often present locally in oxy-coal flames, potentially resulting in enhanced production of NOx if the burner is not suitably designed and operated [12].

A detailed understanding of the interaction of the different formation and destruction routes of NOx during O_2/CO_2 recycle combustion of coal is lacking. In particular, the relative importance of thermal NOx, flame zone reburn of recycled NOx, and NOx reduction on coal char during oxy-coal combustion have yet to be clearly determined. To improve our understanding of these complex interactions, we have performed experiments on NOx formation from combustion of pulverized coal and char particles under isothermal and nearly constant oxygen conditions in a large entrained flow reactor. This unique dataset should provide an unparalleled opportunity to understand and differentiate the different sources and sinks of NOx under oxy-fuel combustion conditions.

2. Experimental Apparatus and Conditions

Experiments were performed in Sandia's Multifuel Combustor (MFC), an electrically heated, down-fired turbulent entrained flow reactor with a length of 4.2 m and an internal flow diameter of 150 mm (see Fig. 1). The basic layout of this facility has been previously described in the literature [13]. To perform experiments on oxy-fuel combustion, the gas supply system for the MFC was modified to provide mixtures of dry air, nitrogen, oxygen, or carbon dioxide, allowing a variety of O_2/N_2 or O_2/CO_2 conditions to be investigated. For the experiments reported here, the natural gas burner on top of the MFC was used to preheat the reactant gases before flowing into the reactant tube where fuel particles were introduced. The natural gas burner can operate slightly oxygen-enriched. Addition of strongly oxygen-enriched gas mixtures just downstream of the burner allows the production of preheated, oxygen-enriched gas mixtures in the MFC.

Through trial-and-error, it was determined that an MFC operating temperature of nominally 1050 °C (1320 K) could be maintained while varying the oxygen content of the gas stream between 10 vol-% O_2 and 40 vol-% O_2 in either N_2 or CO_2. Therefore, a series of experimental conditions were established with dilute coal or coal char loading in the MFC in which the mean oxygen content during combustion nominally matched up with the 12, 24, and 36 vol-% O_2 conditions previously investigated for both coal particle ignition and char combustion kinetics [14-16]. To minimize both the heat released during coal combustion (which modifies the gas temperature profile) and the variation in oxygen content during particle combustion, a lean equivalence ratio of 0.15 was chosen for these experiments. Under these conditions, the oxygen levels before and after coal combustion vary by only 15%, as shown in Table 1.

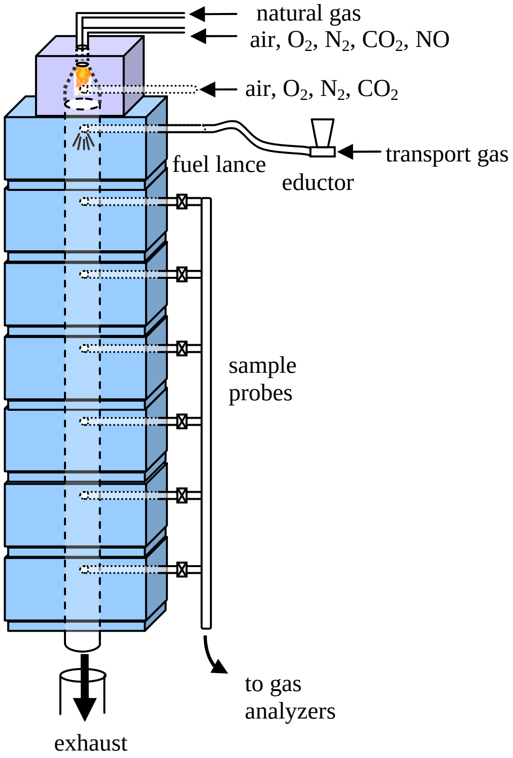

Figure 1: **Schematic illustration of Sandia's Multi-Fuel Combustor, as currently configured for studies of oxy-fuel combustion.**

Table 1. Major Gas Concentrations for NOx Formation Experiments (Pittsburgh Coal)

Nominal Condition	Initial Concentration (vol-%)				Final Concentration (vol-%)			
	O_2	N_2	CO_2	H_2O	O_2	N_2	CO_2	H_2O
12% O_2 in N_2	12.6	75.9	3.9	7.6	10.7	75.7	5.4	8.2
24% O_2 in N_2	25.0	63.5	3.9	7.6	21.2	63.2	6.9	8.7
36% O_2 in N_2	37.6	50.9	3.9	7.6	31.9	50.5	8.3	9.3
12% O_2 in CO_2	13.3	1.1	73.9	11.7	11.3	2.3	74.3	12.1
24% O_2 in CO_2	26.0	1.1	61.2	11.7	22.2	1.2	63.8	12.8
36% O_2 in CO_2	38.7	1.1	48.6	11.7	32.9	1.1	52.6	13.4

Note that we have intentionally chosen experimental conditions to produce NO formation data that are characteristic of combustion of coal particles in a given oxygen-diluent environment. This data should yield greater insight into the governing chemical and physical phenomena controlling NOx formation than the more typical data that have been collected when burning near-stoichiometric mixtures of coal and oxygen-enriched nitrogen or carbon dioxide (akin to actual boiler operation). This latter type of data is useful for tracking overall trends of NO formation in oxy-fuel combustion but yields little scientific understanding because of the wide range of oxygen concentrations (typically ranging from 30+ vol-% O_2 down to a few vol-% O_2) experienced during combustion. Also, the high particle loadings in these latter studies intermix

NO formation and destruction processes, whereas under our dilute loading conditions NO formation processes dominate (at least when the initial NO levels are low). To separately investigate the strength of NO reburning under our low equivalence ratio conditions, experiments were also performed with an elevated level of NO in the gases into which the coal was introduced. For these experiments, the NO concentration entering the MFC was 550 ppm, in contrast to the typical baseline concentration of 30 ppm NO.

A series of silicon carbide probes were used to withdraw gas samples every 0.6 m down the reactor. The sample gas was drawn through heated teflon tubing, maintained at 135 °C, and passed through a heated particulate filter before being analyzed by two separate Horiba gas analysis systems. The gas analysis systems measured the concentrations of CO_2 (NDIR and pyroelectric analyzers), CO (NDIR), NO (NDIR and chemiluminescent analyzers, set for measurement of total NOx), and O_2 (paramagnetic and zirconium oxide analyzers). The results from the two analyzer systems agreed within 5% for all species except NOx, and were within 10% of one another for NOx. The average of the results from the two analyzer systems is shown here.

The coals investigated in this study include Pittsburgh seam coal from the Bailey mine, a typical eastern U.S. medium-sulfur high-volatile bituminous coal, and Black Thunder, one of the most heavily mined low-sulfur Powder River Basin subbituminous coals. These coals were commercially pulverized to meet typical pulverized coal burner specifications (70 wt-% below 200 mesh). Table 2 gives the proximate and ultimate analysis of these coals.

In addition to investigating NO production from burning raw coal, Pittsburgh coal char particles were burned, to evaluate the effect of fuel volatiles on NOx formation and reburn. The char particles were produced by injecting a large stream of coal into the MFC when it was being fed by 2% O_2 at 1500 K and collecting the char particles at the bottom of the MFC with a cyclone with a nominal size cutoff of 10 μm [17]. The char produced in this way had a burnout of 37%, based on ash tracer analysis, and negligible volatile matter, as shown in Table 2. The measured

Table 2. Proximate and Ultimate Analysis of Coals

	Coal Type				Char	
	Pittsburgh Bailey		Black Thunder		Pittsburgh Bailey	
Proximate	wt%, as rec'd	wt% dry	wt%, as rec'd	wt% dry	wt%, as rec'd	wt% dry
moisture	1.4		10.8		1.1	
ash	6.9	7.0	5.0	5.6	19.4	
volatiles	35.4	35.9	40.4	45.3	3.3	
fixed C	56.3	57.1	43.8	49.1	76.2	
Ultimate	wt% dry	wt% DAF	wt% dry	wt% DAF	wt% dry	wt% DAF
C	77.2	82.9	60.9	64.1	76.9	
H	5.2	5.6	5.2	5.5	0.7	
O (by diff.)	7.2	7.7	27.6	29.1	0.2	
N	1.5	1.6	0.9	0.9	1.3	
S	2.0	2.2	0.4	0.5	1.2	

size distribution of the char showed a sharp dropoff between 10 and 20 μm but otherwise was consistent with the size distribution of the raw coal [17].

3. Results and Discussion

Measured gas temperature profiles during combustion of Pittsburgh seam coal, Black Thunder coal, and Pittsburgh seam coal chars are shown in Fig. 2. These profiles demonstrate the relative uniformity and reproducibility of temperature profiles in the MFC for the chosen experimental conditions, even when using different fuels, diluents, and oxygen concentrations. All of the profiles show an early rise because of heat release associated with combustion of the coal or char introduced, with an earlier temperature rise associated with enhanced oxygen levels. (To maintain a consistent equivalence ratio, the fuel loading is increased as the oxygen concentration increases, leading to more heat release into the ~ constant volumetric flow of gases; also, the coal and char particles burnout more quickly with higher oxygen levels.)

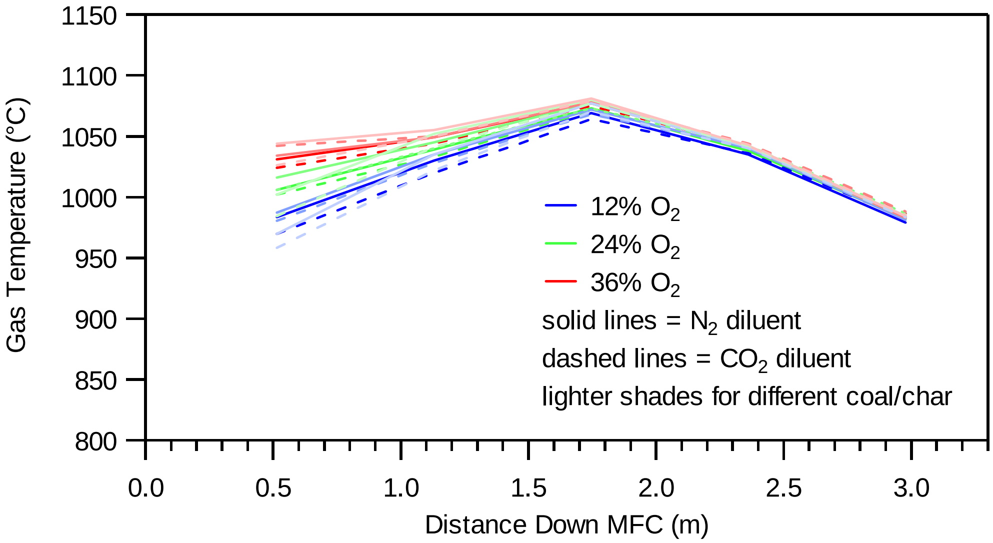

Figure 2: Temperatures measured by type-K thermocouples as a function of distance from the top of the MFC for the investigated conditions.

The measured NOx concentrations in the MFC during coal combustion experiments with low background NOx are shown in Figs. 3 and 4. Measurements of carbon monoxide (CO) show that combustion of the coal is more or less complete by the first sampling location, so only minor variations in NOx are seen with increasing residence time in the reactor. The measured NOx concentrations show a marked increase as the bulk gas oxygen content is increased. For enhanced oxygen levels, combustion in a CO_2 bath gas clearly decreases NOx formation. This is expected because of the lack of thermal NOx production in the N_2-free gas environment. In addition, lower volatile flame temperatures and lower char combustion temperatures in a CO_2 environment should decrease fuel nitrogen conversion to NOx. In general, the Black Thunder coal produces more NOx than the Pittsburgh coal, despite a lower level of fuel nitrogen in the Black Thunder coal (on a DAF basis, there is 0.92 wt-% nitrogen in Black Thunder coal and 1.63 wt-% in the Pittsburgh seam coal). At low oxygen levels (12 vol-% O_2), the NOx levels continuously decrease as a function of residence time in the MFC (after an initial increase from coal combustion), whereas at 24% O_2 the NOx levels stay ~ constant with residence time. At 36% O_2 the NOx levels tend to increase with residence time, especially for the Black Thunder coal.

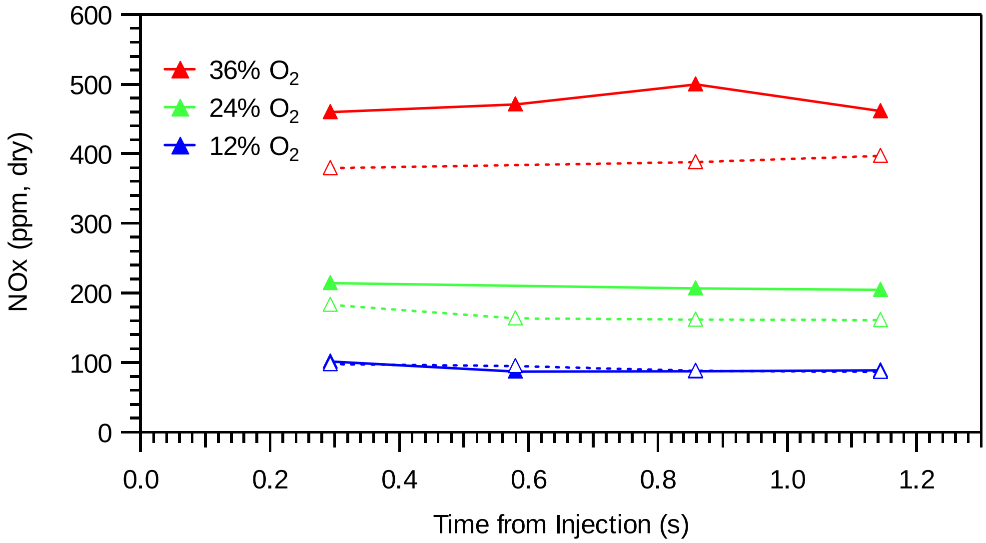

Figure 3: **Measured NOx concentrations during Pittsburgh coal combustion at an equivalence ratio of 0.15 for the stated oxygen levels. Solid lines indicate N_2 diluent, whereas dashed lines are for CO_2 diluent. The initial NO before coal injection is 30 ± 10 ppm.**

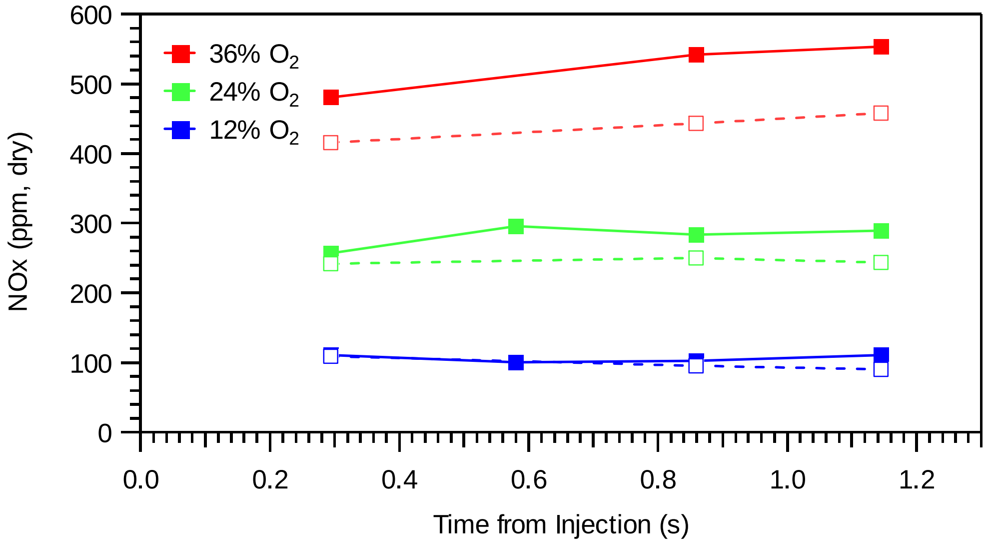

Figure 4: **Measured NOx concentrations during Black Thunder coal combustion at an equivalence ratio of 0.15 for the stated oxygen levels. Solid lines indicate N_2 diluent, whereas dashed lines are for CO_2 diluent. The initial NO before coal injection is 30 ± 10 ppm.**

However, to properly interpret the variation in NOx production as a function of bulk gas oxygen content and solid fuel, one must consider variations in fuel loading for the different flow conditions. Similarly, the higher oxygen content of the Black Thunder coal necessitated a higher mass loading of this coal to attain the same stoichiometry as the Pittsburgh coal. Assuming that most of the NOx is derived from the fuel nitrogen (certainly true in the case of the CO_2 diluent), a more insightful means of analyzing the NOx data is to express it in terms of the fractional conversion of fuel nitrogen to NOx, as shown in Figs. 5 and 6.

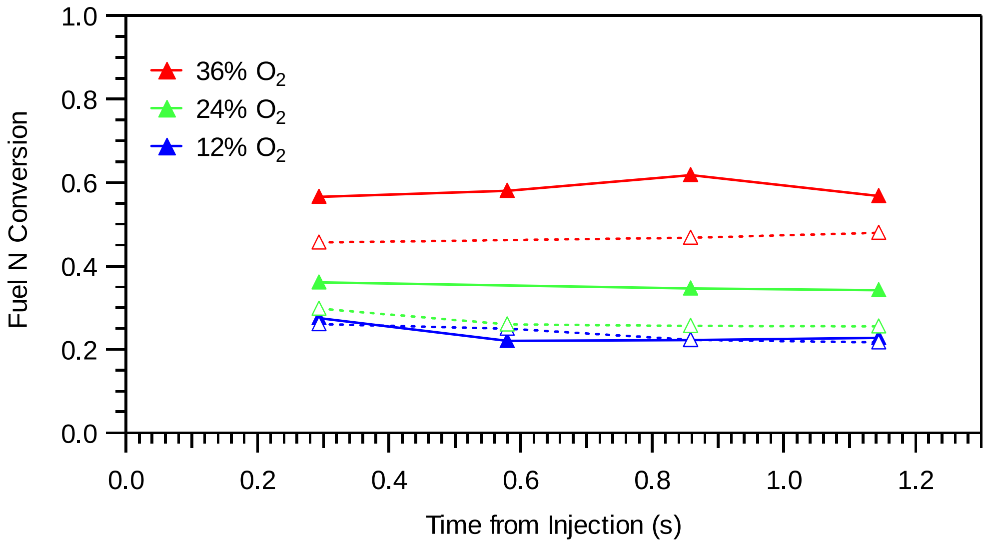

Figure 5: **Fuel nitrogen conversion to NOx during Pittsburgh coal combustion at an equivalence ratio of 0.15 for the stated oxygen levels. Solid lines indicate N_2 diluent, whereas dashed lines are for CO_2 diluent. The initial NO before coal injection is 30 ± 10 ppm.**

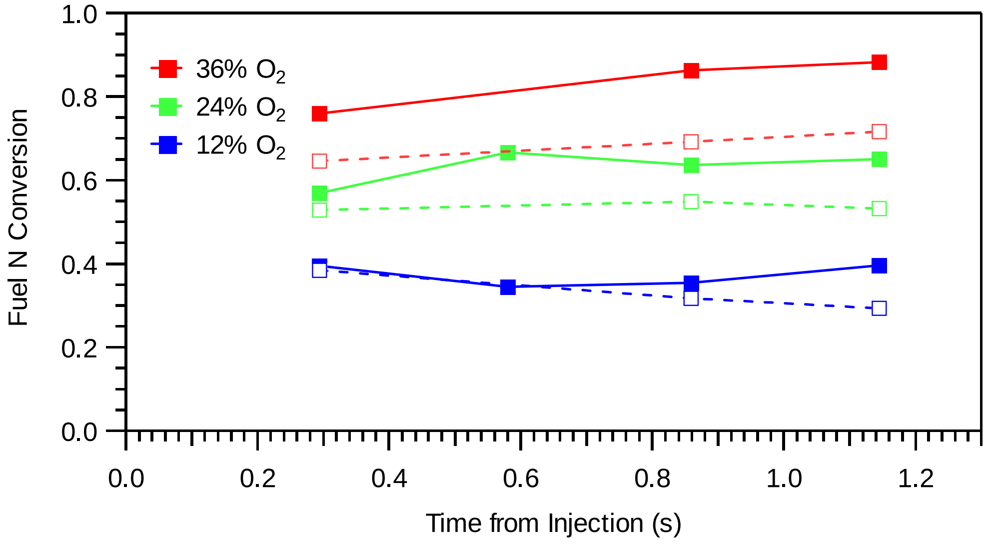

Figure 6: **Fuel nitrogen conversion to NOx during Black Thunder coal combustion at an equivalence ratio of 0.15 for the stated oxygen levels. Solid lines indicate N_2 diluent, whereas dashed lines are for CO_2 diluent. The initial NO before coal injection is 30 ± 10 ppm.**

Figure 5 shows that only 1/5 of the fuel nitrogen is converted to NOx when the Pittsburgh coal particles burn in an atmosphere of 12% O_2. At 24% O_2 approximately 1/3 of the fuel nitrogen is converted to NOx in a N_2 diluent and about ¼ is converted when in a CO_2 environment. At 36% O_2 the conversion factors increase to 55% and 45%, respectively. For the Black Thunder coal, Fig. 6 shows the fuel nitrogen conversion factor is approximately 35% for combustion in 12% O_2, 60% for combustion in 24% O_2, and 80% for combustion in 36% O_2, with similar decreases in conversion factor in CO_2 environments as seen for the Pittsburgh coal. Recall that for these experiments the oxygen content stays relatively constant throughout coal combustion, so that both the volatile flame temperature and the coal char combustion temperature increase as the oxygen level is increased. Therefore, the increase in fuel nitrogen conversion to NOx at higher O_2 levels is not unexpected.

Figures 7 and 8 show NOx formation data for combustion of the Pittsburgh seam coal in comparison to combustion of its char, previously generated under fuel-rich devolatilization conditions in the MFC. Figures 9 and 10 give the corresponding fuel nitrogen conversion data. These figures give a direct indication of the relative contribution of volatile-generated NOx and char-generated NOx under the investigated conditions (ignoring, for the moment, the contribution of the NO-char reaction). The trends in Figs. 7-10 show that volatile-generated NOx is a larger fraction of the total coal-NOx generation at enhanced oxygen levels. This may result from a larger effect of oxygen level on volatile flame temperatures than on char combustion temperatures. The influence of CO_2 on char-NOx formation appears to be of a similar relative magnitude at 24% O_2 and 36% O_2, but appears to have almost negligible influence at 12% O_2, as was also found during combustion of the raw coal particles.

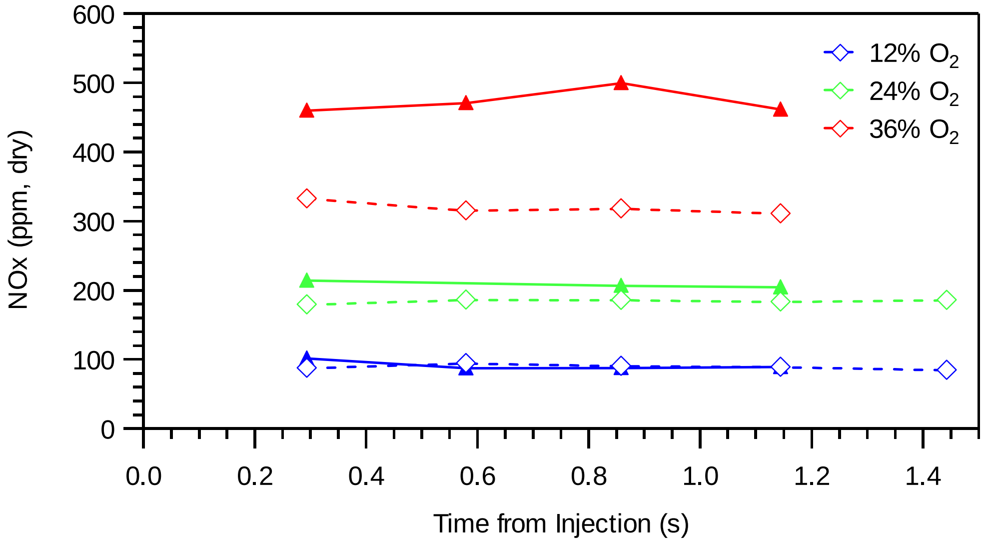

Figure 7: **Measured NOx concentrations during combustion of Pittsburgh coal and Pittsburgh char at an equivalence ratio of 0.15 for the stated oxygen levels in a N_2 background gas. Solid lines indicate the coal, whereas dashed lines are for the char. The initial NO before coal injection is 30 ± 10 ppm.**

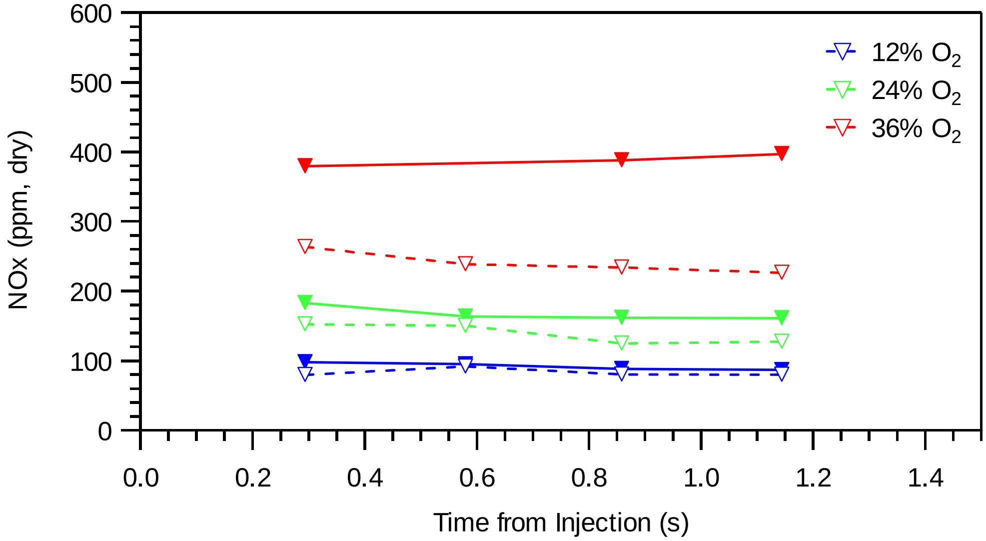

Figure 8: **Measured NOx concentrations during combustion of Pittsburgh coal and Pittsburgh char at an equivalence ratio of 0.15 for the stated oxygen levels in a CO_2 background gas. Solid lines indicate the coal, whereas dashed lines are for the char. The initial NO before coal injection is 30 ± 10 ppm.**

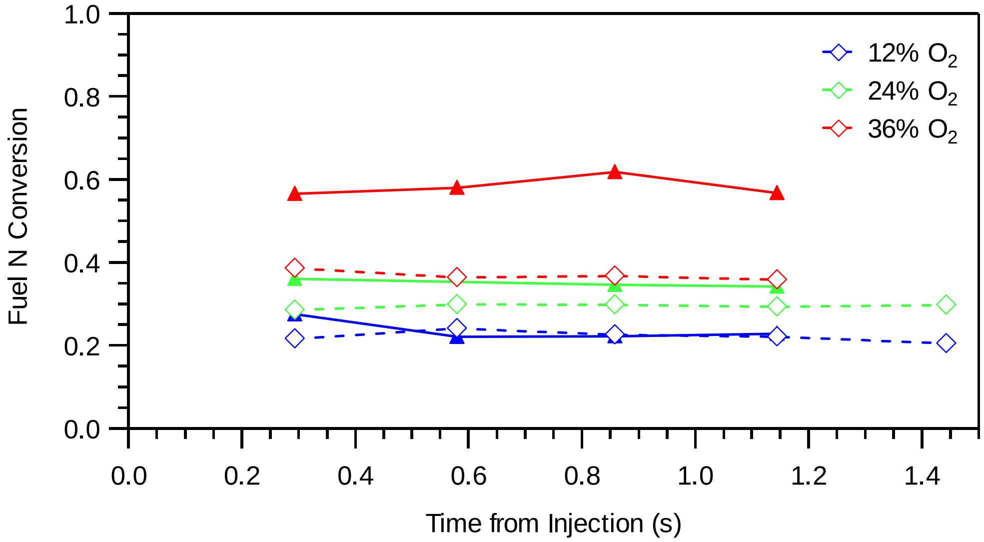

Figure 9: **Fuel nitrogen conversion to NOx during combustion of Pittsburgh coal and Pittsburgh char at an equivalence ratio of 0.15 for the stated oxygen levels in a N_2 background gas. Solid lines indicate the coal, whereas dashed lines are for the char. The initial NO before coal injection is 30 ± 10 ppm.**

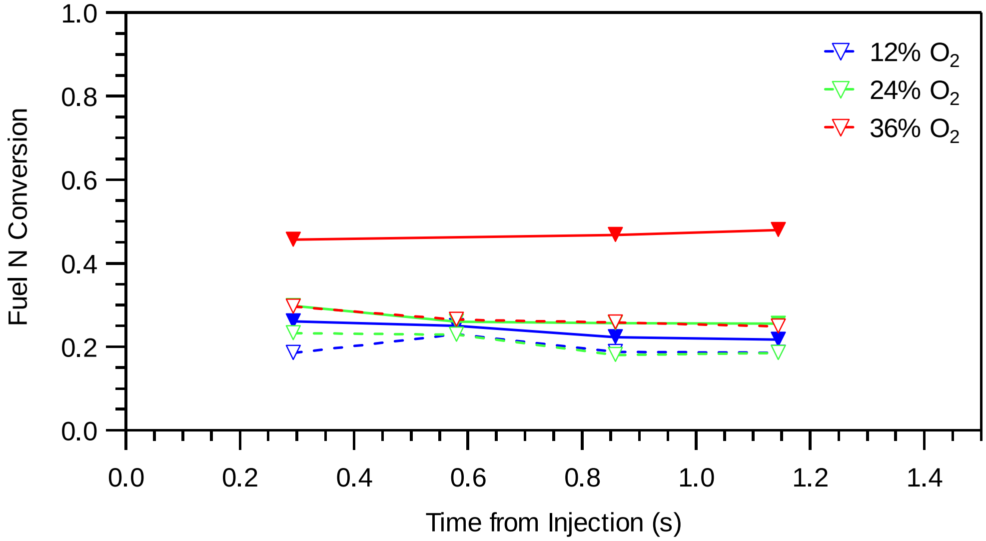

Figure 10: **Fuel nitrogen conversion to NOx during combustion of Pittsburgh coal and Pittsburgh char at an equivalence ratio of 0.15 for the stated oxygen levels in a CO_2 background gas. Solid lines indicate the coal, whereas dashed lines are for the char. The initial NO before coal injection is 30 ± 10 ppm.**

Figure 11 shows the effect of elevated NO concentrations on NOx formation during combustion of Pittsburgh coal at different oxygen levels. In contrast to the previously shown results for low background NO levels, in which coal combustion leads to additional NOx production, at 12% O_2 there is actually a small decrease in the NOx level (i.e. there's net NOx *destruction* during coal combustion) and at 24% O_2 there is essentially zero net NOx production. At 36% O_2 there is

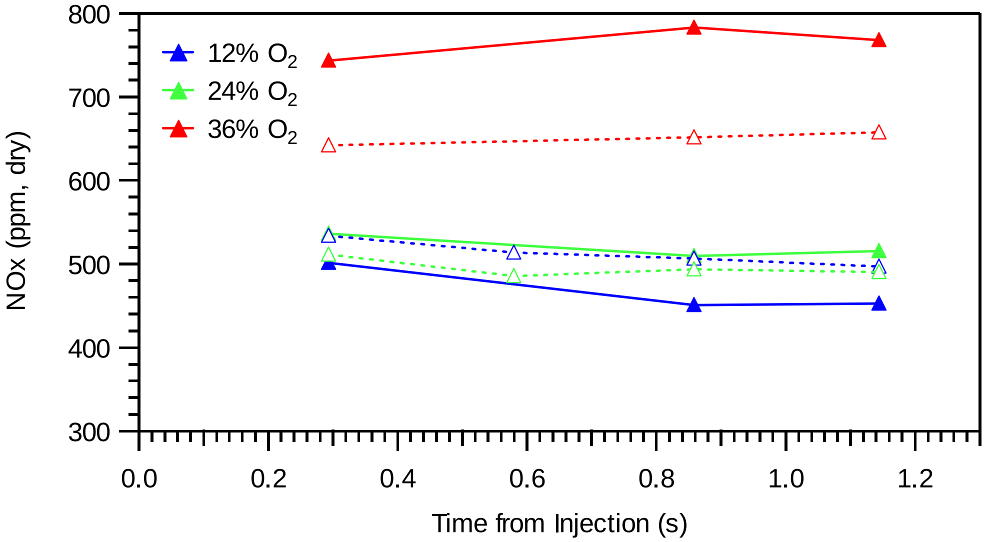

Figure 11: **Measured NOx concentrations during Pittsburgh coal combustion at an equivalence ratio of 0.15 for the stated oxygen levels. Solid lines indicate N_2 diluent, whereas dashed lines are for CO_2 diluent. The initial NO before coal injection is 530 ± 30 ppm for N_2 diluent and 570 ± 80 ppm for CO_2 diluent.**

significant net production of NOx, especially for the N_2 diluent. The calculated fuel nitrogen conversion for this condition is equal to 0.30 for N_2 diluent and 0.14 for CO_2 diluent. Surprisingly, at 12% O_2 the NOx level is higher for combustion in the CO_2 diluent relative to the N_2 diluent.

4. Concluding Remarks

The complex chemistry of NOx formation and destruction during combustion of coal and coal chars necessitates a combination of carefully controlled experimental measurements and modeling analysis. The data presented here should provide an important dataset for comparison with detailed kinetic models. Previous analysis of the influence of a CO_2 bath gas on coal particle ignition and char combustion suggests that it may have a complex role on NOx formation, and the data shown here support that assessment.

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